Republic of South Africa

EDICT OF GOVERNMENT

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SANS 6056 (2007) (English): Water - Sulfide content

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Edition 2

SOUTH AFRICAN NATIONAL STANDARD

Water — Sulfide content

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Table of changes

Change No.	Date	Scope

Foreword

This South African standard was approved by National Committee StanSA SC 5140.19A, *Water – Water sampling and analysis*, in accordance with procedures of Standards South Africa, in compliance with annex 3 of the WTO/TBT agreement.

This document was published in May 2007. This document supersedes SABS SM 1056:1982 (first edition).

Water — Sulfide content

1 Scope

This standard specifies a method for the determination of the sulfide content of water and wastewater.

2 Normative reference

The following referenced document is indispensable for the application of this document. All normative documents are subject to revision and, since any reference to a normative document is deemed to be a reference to the latest edition of that document, parties to agreements based on this document are encouraged to take steps to ensure the use of the most recent edition of the normative document indicated below. Information on currently valid national and international standards can be obtained from Standards South Africa.

SANS 3696/ISO 3696, *Water for analytical laboratory use – Specification and test methods.*

3 Principle

Under suitable conditions a reaction between p-amino-dimethylaniline, ferric chloride, and the sulfide ion results in the formation of methylene blue. Ammonium phosphate is added to remove the colour caused by the ferric ion, and the colour is then visually matched with that of standard methylene blue solutions.

4 Interference

Strong reducing agents interfere by preventing the formation of a blue colour. Thiosulfate at concentrations of about 10 mg/L could retard colour formation or completely prevent it. Ferrocyanide produces a blue colour. Sulfide itself prevents the reaction if its concentration is very high, in the range of several hundred milligrams per litre. Many metals, for example mercury (Hg), cadmium (Cd) and copper (Cu), form insoluble sulfides and give low recoveries.

Eliminate interferences due to sulfite, thiosulfite, iodide, and many other substances, but not ferrocyanide, by first precipitating zinc sulfide (ZnS), removing the supernatant, and replacing it with distilled water (see clause 6).

5 Reagents

5.1 General

Unless otherwise specified, only use water that complies with the requirements for grade 3 water as given in SANS 3696, and reagents of analytical reagent grade.

5.2 Amine-sulfuric acid solution

5.2.1 Stock solution

Distil p-amino-dimethylaniline in an all-glass apparatus from which air has been displaced by an inert gas. Very cautiously mix 50 mL of concentrated sulfuric acid with 30 mL of water and cool. To this add 20 g of the purified amine, stirring until solution is complete. Make up to 100 mL with water.

Alternatively, if p-amino-dimethylaniline sulfate is available in a much purer state than is the amine itself, proceed as follows:

Mix 46 mL of concentrated sulfuric acid with 30 mL of water and cool. To this add 27,2 mL of p-amino-dimethylaniline sulfate, stirring until solution is complete. Make up to 100 mL with water.

NOTE If any of the amine gets on the skin, it should be washed off immediately with dilute hydrochloric acid.

5.2.2 Working solution

Dilute 25 mL of the stock solution to 1 L with the 1+1 sulfuric acid.

5.3 Ammonium phosphate solution

Dissolve 400 g of ammonium phosphate [$(NH_4)_2HPO_4$] in water and make up to 1 L.

5.4 Ferric chloride solution

Dissolve 100 g of ferric chloride ($FeCl_3 \cdot 6H_2O$) in water and make up to 100 mL.

5.5 Standard iodine solution, $c\left(\frac{I_2}{2}\right)$ = 0,025 mol/L

Add 3,175 g of iodine to about 25 g of potassium iodide and moisten with water. Slowly add more water (with shaking) until the mixture has dissolved, dilute to 1 L, and standardize against the sodium thiosulfate working solution (see 5.9.2)

5.6 Methylene blue solutions

5.6.1 Strong solution

5.6.1.1 Preparation

Dissolve 1,0 g of methylene blue in water and make up to 1 L. Standardize the solution as in 5.6.1.2.

5.6.1.2 Standardization

5.6.1.2.1 Completely fill a 5 L bottle with acidified water, add a washed crystal of sodium sulfide (about 100 mg to 200 mg), stopper the bottle, and then mix thoroughly.

5.6.1.2.2 Pipette 20 mL of the standard iodine solution into a 500 mL volumetric flask.

5.6.1.2.3 Siphon in enough sulfide solution from the bottom of the 5 L bottle to fill the flask to the mark.

5.6.1.2.4 Transfer the contents to a suitable beaker, add 1 mL of concentrated sulfuric acid and titrate the excess iodine with the sodium thiosulfate working solution (see 5.9.2) using starch as an indicator.

5.6.1.2.5 Multiply the net volume of the standard iodine solution used by 0,835 to obtain the concentration of sulfide in milligrams per litre.

5.6.1.2.6 Test the sulfide solution by the procedure given in clause 4 and adjust the strength of the methylene blue solutions to give the same value for the concentration of sulfide as that obtained by the titration method.

5.6.2 Dilute solution

Dilute 10 mL of the strong solution to 100 mL with water.

5.7 Standard potassium dichromate solution, $c\left(\frac{K_2Cr_2O_7}{6}\right)$ = 0,025 mol/L

Dissolve 1,226 g of previously dried potassium dichromate ($K_2Cr_2O_7$) in water and dilute to 1 L.

5.8 Sodium hydroxide solution

Dissolve 9 g of sodium hydroxide in water. Cool and dilute to 100 mL.

5.9 Sodium thiosulfate

5.9.1 Stock solution, $c(Na_2S_2O_3)$ = 0,25 mol/L

Dissolve 63 g of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$), in 1 L of freshly boiled and cooled water, adding 1 mL of chloroform or 10 mg of mercuric iodide to stabilize the solution. Allow to stand for several days before use.

5.9.2 Working solution, $c(Na_2S_2O_3)$ = 0,025 mol/L

5.9.2.1 Preparation

5.9.2.1.1 Dilute 100 mL of the stock solution to 1 L with freshly boiled and cooled water, adding 1 mL of chloroform or 10 mg of mercuric iodide.

5.9.2.1.2 Store in an amber glass bottle with a rubber stopper, and standardize as in 5.9.2.2 at frequent intervals.

5.9.2.1.3 Discard any solution remaining in the burette at the end of the day.

5.9.2.2 Standardization

5.9.2.2.1 Dissolve approximately 2 g of potassium iodide (KI) free from iodate in 100 mL to 150 mL of water in an Erlenmeyer flask, add 10 mL of 1+9 sulfuric acid followed by exactly 20 mL of the standard potassium dichromate solution.

5.9.2.2.2 Place in the dark for 5 min, dilute to about 400 mL and titrate with thiosulfate until a pale straw colour is reached, then add the starch solution (see 5.10) and titrate until colourless.

5.9.2.2.3 If the sodium thiosulfate concentration is not exactly 0,025 mol/L, adjust it until it is.

5.10 Starch solution

Grind 0,5 g of soluble starch into a smooth paste with 10 mL of cold water and stir the resultant paste into 200 mL of boiling water. Boil for 1 min and allow to cool. Use freshly prepared.

5.11 Sulfuric acid

Dilute 1:1 solution. Mix very cautiously equal volumes of concentrated sulfuric acid and water.

5.12 Zinc acetate solution

Dissolve 220 g of zinc acetate solution [$Zn(C_2H_3O_2)\cdot 2H_2O$] in 870 mL water to make up 1 L of solution.

6 Test sample

6.1 Prevent the loss of free hydrogen sulfide by the addition to the sample on collection of 0,20 mL (four drops) of zinc acetate solution.

6.2 Ensure that errors are not introduced by the following:

a) loss of sulfide by direct oxidation with admitted oxygen; and

b) formation of hydrogen sulfide due to storage of the sample under anaerobic conditions.

7 Apparatus

7.1 **Test tubes**, two with identical diameters.

7.2 **Pipette**, standard dropping, capable of delivering 20 drops/mL.

7.3 **Burette**, 1 mL.

8 Procedure

8.1 As soon as possible after the test sample is taken, pipette 7,5 mL of the sample into each of the two test tubes. If the sample has been preserved with zinc acetate, shake vigorously before taking the subsample.

8.2 To the first tube add 0,5 mL of the amine-sulfuric acid working solution.

8.3 To the second tube add 0,5 mL of the dilute sulfuric acid. Add two drops of the ferric chloride solution to each tube, close them with the thumbs and slowly invert them once or twice to mix the contents. When sulfide is present a blue colour will appear in the first tube; colour development is complete after approximately 1 min.

8.4 After 2 min to 5 min, add 1,6 mL of the ammonium phosphate solution to each tube and mix.

NOTE This diminishes the colour caused by the ferric chloride and reduces the acidity of the solution enabling a more intense blue colour to form.

8.5 After 5 min add methylene blue solution a drop at a time to the second of the two tubes, mixing between each addition, until the colour matches that of the first tube. Add the solution either from the standard dropping pipette or from the burette. If the methylene blue is of the correct strength, one drop of the strong solution (0,05 mL) is equivalent to 1 mg/L of sulfide and one drop of the dilute solution is equivalent to 0,1 mg/L of sulfide.

8.6 For highest accuracy add an equal volume of water to the first tube before the colours are matched, thus eliminating any error due to the increased volume in the second tube.

9 Expression of results

Express the results as follows:

Sulfide content (S) in milligrams per litre.